LLNL-JRNL-667217

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February 10, 2015

Journal of Chemical Physics

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Influence of single particle orbital sets and configuration selection on multideterminant wavefunctions in quantum Monte Carlo

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Abstract

Multideterminant wavefunctions, while having a long history in quantum chemistry, are increasingly being used in highly-accurate quantum Monte Carlo calculations. Since the accuracy of QMC is ultimately limited by the quality of the trial wavefunction, multideterminants offer an attractive alternative to Slater-Jastrow and more sophisticated wavefunction ansatzs for several reasons. They can be efficiently calculated, straightforwardly optimized, and systematically improved by increasing the number of included determinants. In spite of their potential, however, the convergence properties of multislater jastrow wavefunctions with respect to orbital set choice and excited determinant selection are poorly understood, which hinders the application of these wavefunctions to large systems and solids. In this paper, by performing QMC calculations on the equilibrium and stretched carbon dimer, we find that convergence of the recovered correlation energy with respect to number of determinants can depend quite strongly on basis set and determinant selection methods, especially where there is strong correlation. We demonstrate that properly chosen orbital sets and determinant selection techniques from quantum chemistry methods can dramatically reduce the required number of determinants (and thus the computational cost) to reach a given accuracy, which we argue shows clear need for an automatic QMC-only method for selecting determinants and generating optimal orbital sets.

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I. INTRODUCTION

The successful use of computational methods in the study of material properties has dramatically increased over the last decade, due in part to the success of mean-field methods like density functional theory (DFT). By approximately treating electronic correlation effects through an "exchange-correlation functional", DFT offers an excellent ratio between cost and accuracy, leading to its current position as the main workhorse in electronic structure and first-principles simulations. However, for systems that require a very accurate description of electronic correlation, improving the exchange-correlation functional is nontrivial and far from systematic, making highly accurate many-body methods increasingly attractive as computational resources exponentially increase.

Of these many-body methods, projector Quantum Monte Carlo (p-QMC) [1, 2] is especially attractive due to its high accuracy and modest computational cost, which it achieves through stochastically projecting and sampling the ground-state wavefunction of Schrödinger's equation. The fundamental limitation on the accuracy of projector QMC methods for realistic systems is the "fixed-node approximation". Here, we *assume* that the nodes of our many-body ground-state wavefunction Ψ_0 are identical to those of an antisymmetric trial wavefunction Ψ_T. The p-QMC algorithm then projects out the lowest energy fermionic ground-state consistent with these boundary-conditions in polynomial time, in contrast to the exact algorithm which suffers from the "fermion sign-problem" and associated exponential scaling.

In standard-practices QMC, the nodes of the many-body wavefunction are taken to be equivalent to those of a single slater determinant, built up from single-particle orbitals taken from a mean field theory like Hartree-Fock or density functional theory. Despite the simplicity of this nodal ansatz, experience dictates that this approximation is exceptionally good at capturing the majority of electronic correlation effects across a large range of systems. For non-covalent interactions, QMC has been shown to describe interactions in dimers[3] and water clusters[4, 5] about as well as the best traditional quantum chemistry methods (e.g. coupled-cluster theory with singles, doubles, and perturbative triples CCSD(T)). For solids, benchmarking of the bulk modulus and equilibrium unit cell volume indicate that DMC is very competitive with state-of-the-art density functionals across a range of covalent, ionic, and van der Waals solids[6]. Various benchmarks against experiment on the G2 test set[7] indicate that single-determinant DMC obtains a mean-absolute deviation of between 2.1[8] and 2.9 kcal/mole[9, 10] for atomization energies, which is on par with CCSD(T) when using a cc-pVQZ basis set.

With the introduction of robust optimization methods capable of simultaneously optimizing thousands of non-linear parameters, the prospect of being able to reduce the fixed-node error through massively parameterized and systematically improvable wavefunction ansatzs is becoming feasible. Though there are several promising classes of wavefunctions that might meet this criterion, for example AGP[11], Pfaffians [12], LVB's[13], multideterminant expansions possess several advantages that make them quite promising. First, they have been shown to be extremely accurate. DMC benchmarks over the G2 test set of various trial wavefunctions based on multideterminant expansions have finally produced sub-chemical accuracy for atomization energies, and near chemical accuracy for total energies [8, 10]. For first row atoms and dimers, MSD's are able to routinely recover at least 99% of correlation energies [10, 14, 15]. MSD's have also been shown to be able to accurately describe the dissociation of the C2 and N2 dimers[16].

MSD based QMC algorithms possess some nice properties in contrast to other wavefunction forms. First, there exist fast update formulae and compression algorithms for MSD's, which do not significantly affect the scaling of the QMC algorithm[17–19]. Second, optimization is fairly stable, since the expansion is built up from a linear combination of slater determinants with variable coefficients. Third, much like in traditional QMC calculations where mean-field calculations help construct a starting ansatz for the slater determinant, traditional quantum chemistry methods can be used to construct a reasonable starting guess for single-particle orbitals and important determinants. Lastly, once we have a procedure for constructing excited determinants, the number of included determinants becomes an adjustable parameter that will eventually converge to the correct result in the limit that we include all possible determinants. In practice, even the inclusion of tens to hundreds of determinants typically leads to significant improvements in the resulting trial wavefunctions.

Whereas in quantum chemistry, there are well studied and employed prescriptions for building accurate and compact multideterminant wavefunctions, similar studies have not been performed in QMC. To remedy this, we propose in this paper to systematically investigate the impact that common orbital choices and methods of choosing determinants has on the fixed-node error in the equilibrium and stretched carbon dimer. Not only does this system possess a significant amount of static correlation (even in equilibrium), but there exist highly accurate full CI calculations describing ground and excited state energies from equilibrium all the way to the dissociation limit [20, 21]. After discussing the computational details, we will investigate how the fixed-node energy changes at the single-slater and MSD level with respect to orbitals taken from methods like Hartree-Fock, DFT, and multi configuration self-consistent field methods (MCSCF). We will also investigate how quickly common methods of generating determinant expansions converge–specifically CISD, CISDTQ, and SOCI. With this information in hand, we then discuss which methods produce lowest and most rapidly converging energies within the QMC framework, analyze the relevant physics responsible for this behavior, and then discuss how these observations relate to extending MSD wavefunctions to solids.

II. COMPUTATIONAL DETAILS

In this section, we will describe the generation of single-particle orbitals and the schemes used in the generation and selection of configuration state functions (CSF). Quantum chemistry calculations were performed with the GAMESS package [22, 23]. All results reported in this article, including both QMC and quantum chemistry calculations, used Burkatzki-Fillipi-Dolg (BFD) energy-consistent effective core potentials (ECP) to represent carbon along with the associated basis sets [24, 25]. Unless otherwise stated, we used the BFD basis set consistent with cc-pV5Z.

A. QMC

Our trial wavefunction ansatz will be of the "multi-slater jastrow form", which is expressible as follows:

$$\Psi_T = e^{-J} \sum_{k=0}^{N} \alpha_k \Phi_k \tag{1}$$

Here J is a symmetric Jastrow term, and the set $\{\Phi_k\}$ are antisymmetric configuration state functions (CSF). These are spin and space adapted linear combinations of Slater determinants, and are used because they dramatically cut down on the number of degrees of freedom for our wavefunction parameterizations. They can be written as

$$\Phi_k = \sum_{i=0}^{N} c_i^k \det(M_i^{\uparrow}) \det(M_i^{\downarrow}) \quad (2)$$

Here, $M_i^{\uparrow(\downarrow)}$ is the slater matrix for the up (down) electrons, whose elements are $[M_k^{\uparrow(\downarrow)}]_{ij} = \phi_j(r_i^{\uparrow(\downarrow)})$. The ϕ_j are single particle orbitals taken from the set $\{\phi_0 ... \phi_N\}$. The set of coefficients $\{c_i^k\}$ are fixed by symmetry.

For J(R), we use a sum of spin-dependent two and three-body terms and a spin-independent one-body term. For the one and two body spin-dependent terms, we used a radially symmetric b-spline functional form with 10 knots and a cutoff radius of 10 bohr. For the three-body term, we used standard electron-electron-ion terms with radially symmetric functions expanded in third order polynomials. No electron-ion cusp condition needs to be applied to any of the jastrow terms, since we are using BFD ECPs which are finite at the origin.

Given a set of CSF's $\{\Phi_0 ... \Phi_{N_{CSF}}\}$ built from a set of single-particle orbitals $\{\phi_0 ... \phi_{N_{orb}}\}$, we use the linear method [26, 27] to minimize the VMC energy of Ψ_T with respect to all Jastrow parameters and the CSF coefficients. We performed 16 iterations of energy minimization, using 128,000 samples for the first 10, and 640,000 for the last 6. This typically leads to VMC energies converged to within 0.5 mHa.

Once we had a VMC optimized trial wavefunction, we performed an extended diffusion monte carlo simulation. We determined after performing a time-step extrapolation and population study that a time step of $\tau = 0.005 Ha^{-1}$ and a walker population of 2560 was sufficient to ensure a systematic error of less than 0.2 mHa, which is comparable to the statistical error in our simulations. We used single-particle moves and collected data over 250,000 sweeps.

All optimizations and QMC simulations were performed using the QMCPACK software package [28, 29]. MSD evaluations and updates were accomplished using the fast-update algorithm of Clark et. al. [17].

B. Orbitals

To generate the orbitals, we considered an array of mean-field and many-body methods within the GAMESS quantum chemistry code. Restricted closed-shell Hartree-Fock calculations were initially performed on both the equilibrium and stretched geometries. The orbitals produced from this method we will denote ”HF” in the paper. We also used a semi-local gradient corrected functional, PBE [30], and a hybrid exchange functional, B3LYP[31], to generate single particle orbitals within the density-functional theory framework, which we will reference as “PBE” and “B3LYP” in the paper. We chose these as they represent popular choices and classes of functionals used in the community.

Going beyond mean-field, we used second order Møller-Plesset perturbation theory from the Hartree-Fock solution to get the first order variation in the many-body wavefunction. From the one-body density matrix calculated with MP2, we obtained natural orbitals, which we denote “MP2NO” in the paper.

Lastly, we derived orbitals from two different multiconfigurational self-consistent field methods (MCSCF). The first method we used was CASSCF with an active space consisting of 8 electron in 8 active orbitals. The orbitals resulting from this method, we will denote as “CASSCF(8,8)”, represent near optimal orbitals for the states included in the active space, while orbitals outside this space are not optimized. The second method starts from the same complete active space (CAS) as before, but considers all single and double excitations out of all the determinants in the CAS into a 50 orbital virtual space. We then perform a self-consistent orbital and CSF coefficient optimization. This procedure, known as second order configuration interaction (SOCI), leads to nearly optimal orbitals in the CAS while at the same time optimizing orbitals in the virtual space included in the calculation. The resulting virtual orbitals should not be optimal, but should be considerably improved compared to any of the other methods considered in this article. We will refer to the orbitals generated from this method as “SOCI(8,8)”, which should represent the best orbitals in the set.

C. Choosing the CSF’s

Once we have a set of orbitals, the question then becomes how we should choose the CSF’s to use in our trial wavefunction. As the number of possible CSF’s grows combinatorically with the size of our basis set, searching the full CI space is prohibitively expensive. Instead, we will restrict our attention to various truncated CI spaces, which restricts the number of CSF’s to a reference state and all those accessible by some maximum number of excitations into a set virtual orbital space.

As the number of CSF's in such a space is still often too large for practical QMC calculations, our approach will be to first solve the problem with a particular form of truncated CI or multi-reference CI with a finite virtual space, which gives us $\Psi_{CI} = \sum_k \alpha'_k \Phi_k$. Using the CSF coefficients from this method, we include in our trial wavefunction all CSF's where the magnitude of the coefficient is larger than some cutoff $|\alpha'_i| > \alpha_{cut}$. Notice that the weight of a particular CSF is completely dependent on the orbital set used in the expansion.

The single reference truncated CI methods we will use are CISD and CISDTQ. CISD starts from a single reference determinant, and considers a determinantal subspace spanned by all determinants that differ from the reference by a single or double excitation into the virtual orbital space. The CISDTQ is similar, but in addition considers triple and quadruple excitations into the virtual orbital space.

The main multi-reference CI method we will use is second-order CI, which is the same as the SOCI method described in the orbital section. The key difference from that section is that we will refrain from orbital optimization, taking the orbitals as they are from some other level of theory. In this terminology, SOCI(8,8) with "SOCI(8,8)" orbitals would be equivalent to the full SCF solution.

D. Extrapolations

The previous method gives us a way of selecting a subset of our chosen truncated CI space deemed important by quantum chemistry. We are also concerned with what the fixed-node energy would be in the limit that we included all determinants in some given truncated CI space. Ideally, we should be able to consider the fixed-node energy of several trial wavefunctions constructed using different subsets of CSF's of varying sizes, and use this information to extrapolate to the limit that we include all CSF's in our trial-wavefunction. One natural parameter that we will use is the number of included determinants, although as will become obvious, the number of determinants with significant weights will be an exceedingly small fraction out of all determinants in the trial wavefunction. Since we are using quantum chemistry methods to screen determinants, Umrigar *et. al* [26, 27] pointed out that we can instead consider the sum of squares for the quantum chemistry CSF coefficients corresponding to the CSF's included in the trial wavefunction. Formally, this is written as $|\mathcal{N}|^2 = \sum_{i \in w} |\alpha'_i|^2$, and has the nice property that $|\mathcal{N}|^2 \rightarrow 1$ as we include all determinants in the determinantal subspace. Consistent with previous work[26, 27], this leads to reliable extrapolation of both VMC and DMC energies and we will rely on such extrapolations to obtain converged results in this paper.

E. Reference Energies

Exact energies were estimated using a combination of FCIQMC and CCSD(T) calculations. The FCIQMC method performs a stochastic full configuration interaction calculation and has been shown to be extremely accurate [32–34]. While it is currently limited to small systems, it provides very accurate results (typically within 0.1 mHa of exact results) for system sizes too large for traditional FCI approaches. A recent article by G. Booth *et. al.* [35] makes a detailed analysis of the dissociation curve of the carbon dimer showing essentially exact results for various atomic basis sets, an estimate of the CBS limit is also provided. Table II E shows the energy difference between their FCIQMC results and CCSD(T) calculations as a function of basis set. While the convergence of the total energy is slow with basis set and requires basis set extrapolation techniques for converged results, the convergence of energy differences between these two methods converges quickly with basis set. As a result, we estimate the exact energies at the two studied dimer configurations from a combination of extrapolated CCSD(T) energies and differences between FCIQMC and CCSD(T) at an appropriate finite basis set. In other words we define: $E_{exact} = E_{CCSD(T)-CBS} + \Delta E^{TZ}$, where $\Delta E^{TZ} = E^{TZ}_{FCIQMC} - E^{TZ}_{CCSD(T)}$. We were unable to use the results of G. Booth, *et. al.* [35] directly because they do not use BFD ECPs in the calculations and they only provide results for the $X^1\Sigma_g^+$ state. As we see below, the ground state of the stretch configuration is $B^1\Delta_g$. As a result, we performed our own FCIQMC [39] calculations with the corresponding BFD ECPs used in this study using a code developed by one of the authors. We also provide FCIQMC results without using BFD ECPs to compare against the results reported by G. Booth, *et. al.*.

III. CARBON DIMER

The carbon dimer is a well known difficult test case for ab-initio quantum chemistry methods. Even in its equilibrium geometry, the ground-state of the carbon dimer possesses

	cc-pVDZ	cc-pVTZ	cc-pVQZ
Equilibrium: no ECP $X^1\Sigma_g^+$			
Booth, *et al.*	-	-1.86(2)	-1.70(8)
this study	-1.85(1)	-1.84(2)	-
Equilibrium: BFD-ECP $X^1\Sigma_g^+$			
this study	-1.79(2)	-1.78(2)	-
Stretched: BFD-ECP $B^1\Delta_g$			
this study	-6.7(1)	-6.9(1)	-

TABLE I: Energy difference (in mHa) between FCIQMC and CCSD(T) calculations for the carbon dimer at the two configurations used in this study. The dimer at the equilibrium configuration (R=1.24253 Ang) has an electronic ground state state of symmetry $X^1\Sigma_g^+$, while the stretched configuration (R = 1.8 Ang) has a ground state with symmetry $B^1\Delta_g$. Booth, *et al.* represent FCIQMC results from Ref. [35].

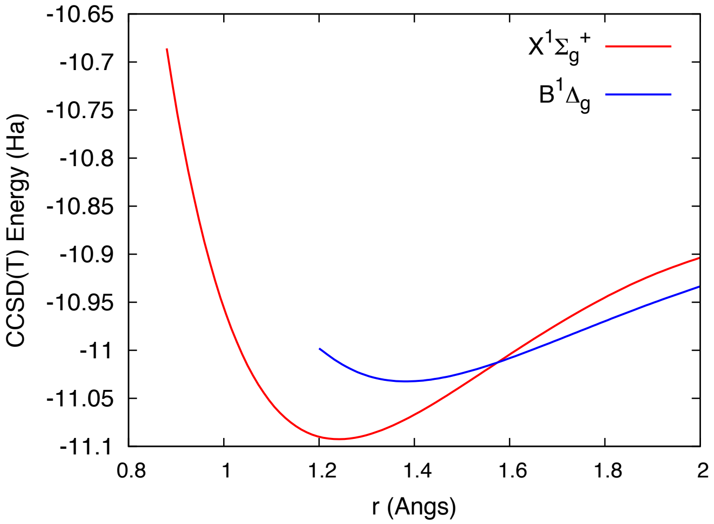

FIG. 1: (Color Online) CCSD(T) energies of the $X^1\Sigma_g^+$ and $B^1\Delta_g$ states of the carbon dimer. Results were obtained using a BFD ECP and a cc-pVQZ atomic basis set.

some multi-reference character [20, 21]. For stretched configurations, after stretching beyond 1.6Å, the combination of an avoided level crossing and near degeneracies (level crossing too) between the ground state and low lying excited states causes a break down of single-reference methods. Figure 1 shows the CCSD(T) energy of the $X^1\Sigma_g^+$ and $B^1\Delta_g$ states as a function of atomic distance, using the BFD ECP and an cc-pVQZ atomic basis set, along with the level crossing around R∼1.6Å. For these reasons, the C2 dimer is an excellent simple system by which we can diagnose problems in our nodal surface.

For both the equilibrium (R=1.2424 Ang) and stretched (R=1.8 Ang) geometries, we will investigate three major properties related to the choice of orbitals and determinants used in our multislater expansion. First, we will investigate the influence of orbital sets on the single determinant DMC energies. This will help us understand any fundamental difference (or lack of) on the nodal structure of the reference determinant in each orbital set. Then, we will look at how the choice of orbitals used in the multi-slater determinant construction affects the ultimate accuracy of the DMC calculations. In this case, since we are only interested on the influence of the orbital set, we use the best configuration selection scheme to construct the trial wave function. Finally, we study the combined influence of orbital set and configuration selection on the ultimate accuracy of DMC energies.

A. Equilibrium Configuration

To begin the discussion of the equilibrium carbon dimer, we look at the fixed-node energies of various single Slater-Jastrow type wavefunctions, presented in Table III A. These DMC calculations differ only on the choice of single-particle orbitals used in the determinant. We find that Hartree-Fock orbitals recover the smallest amount of correlation energy at about 87.2%. We gain about 1% of the correlation energy by instead using MP2 natural orbitals with 88.3%, and then another 0.4-0.5% with PBE, BLYP, CASSCF, or SOCI orbitals, these last four being statistically indistinguishable from one another. Though we can conclude from this that DFT and higher order quantum chemistry methods yield lower energies and thus better nodes than Hartree-Fock or MP2, we see that at the single Slater-Jastrow level, DMC is relatively insensitive to the choice of basis set, having a spread of only 1.7% of the correlation energy for all orbitals considered. Not only this, but we are still missing approximately 11% of the correlation energy of the C2 dimer.

Now we consider the impact that orbital choice has on the quality of multi-slater determinant wavefunctions. To identify "important determinants" to include in our multideterminant wavefunction, we solved the equilibrium C2 dimer using SOCI(8,8) using the

Method	Total Energy (Ha)	% CE
SD-DMC-HF	-11.0494 (4)	87.2
SD-DMC-CASSCF	11.0561 (3)	88.8
SD-DMC-MP2NO	-11.0541 (4)	88.3
SD-DMC-PBE	-11.0565 (2)	88.9
SD-DMC-B3LYP	-11.0556 (3)	88.7
SD-DMC-SOCI	-11.0556 (7)	88.7
CCSD(T)-CBS	-11.10067	99.6
Estimate-Exact	-11.10244(2)	100.0

TABLE II: Energy of the carbon dimer at the equilibrium bond length from single determinant DMC calculations using orbitals generated from a selection of methods. The method abbreviations are described in the text. CCSD(T)-CBS refers to CCSD(T)-R12 calculations obtained from a 3-point extrapolation to the complete basis set limit using cc-pV[T,Q,5]Z basis sets. Estimated-exact results are also included, which were obtained from corrections to CCSD(T) calculations obtained from the FCIQMC method [35]. The percentage of the correlation energy recovered by each method is also presented.

orbitals taken from one of the previously mentioned mean-field or quantum chemistry methods. SOCI(8,8) represents the best method to select CSF's considered in this work (we will cover this in more detail later), so selecting CSF's using this method allows us to focus on the quality of the orbital set and its influence on the final DMC energies.

For all the orbitals tested at the single slater determinant level, we show in Figure 2 the dependence of the fixed node energy on both the CI wavefunction norm (as described in section II D), and the number of CSF's used in our multi-slater determinant wavefunction. The different colors denote the different choice of orbitals, and the black line denotes the reference taken from a CCSD(T) calculation extrapolated to the complete basis set limit. Not surprisingly, the inclusion of only a few CSF's dramatically lowers the fixed-node energy, allowing us to recover an additional 7.5% of the correlation energy beyond the single slater-jastrow level. Extrapolating on the norm of the truncated wave function (to the limit of a full SOCI(8,8) wave function) we find that all orbitals sets result in DMC energies within 4

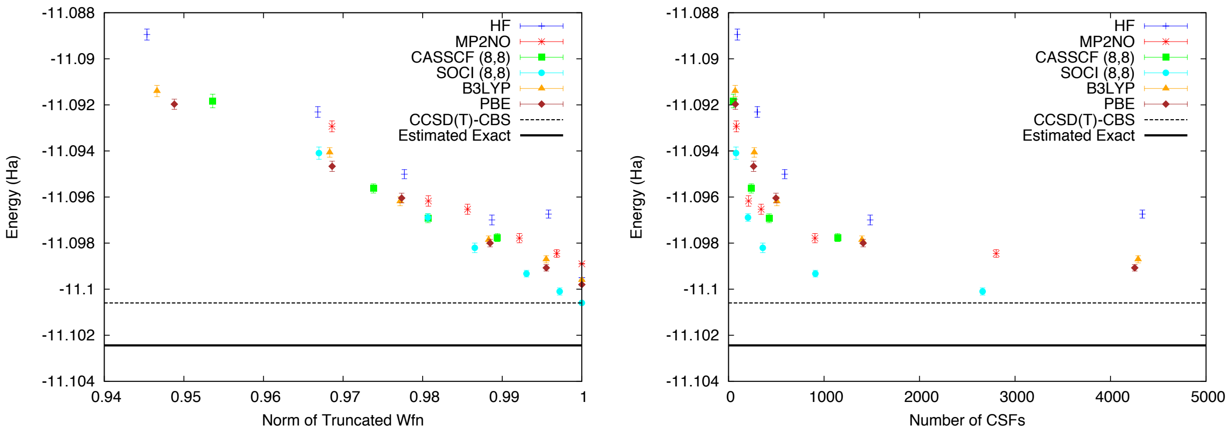

FIG. 2: (Color online) DMC energy of the carbon dimer in the equilibrium configuration as a function of the norm of the truncated trial wave function (left) and as a function of the number of CSFs (right). Results are shown for all the molecular orbital sets considered in this work. CCSD(T)-CBS and estimated exact results are also when for comparison.

mHa of the exact answer. As expected, the best choice is the SOCI(8,8) orbitals, which are about 2mHa away from the exact result, and the worst being MP2, which is 4mHa higher. Overall this example seems to indicate that, as along as we perform an aggressive search of important configurations in the FCi space, the quality of the orbital set is not very relevant in the resulting extrapolated energies. While this is a trivial statement in principle, since a FCI calculation (and the resulting wavefunction) is independent of the molecular orbital set, the fraction of determinants included in our calculations in a negligibly small fraction of the omelet FCI space. This is particularly true in the limit of very large basis sets, which are needed to obtain converged correlation energies in orbital based approaches. A final point that must be discussed is the convergence of the DMC energy as a function of the number of CSFs included in the calculation. While all orbital sets lead to similar extrapolated energies, the rate of convergence can be quite different. In this example, the use of nearly optimal SOCI(8,8) orbitals leads to energies within 4 mHa of the exact answer with just ∼350 CSFs, while HF orbitals required over 2000-3000 CSFs for a similar accuracy. This, of course, merely shows the fact that SOCI(8,8) orbitals have been optimized for a compact CI representation through the SCF approach. Nonetheless, this provides clear justification for the search of optimized orbital sets directly within a QMC framework.

Having looked at how the convergence of the fixed-node energy depends on choice of orbitals, we lastly consider how the convergence depends on the method used to generate excited determinants. In other words, how to select configurations given an orbital set. We consider selecting determinants from CISD, CISDTQ, and SOCI(8,8), using virtual orbital spaces of both 20 and 50 orbitals for all methods. Figure 3 shows the convergence of the fixed-node energy with respect to number of CSF's (top) and norm of the MSD wavefunction (bottom) using HF orbitals (first column), B3LYP orbitals (second column), and SOCI orbitals (last column). The different colors represent the different quantum chemistry methods for choosing the excited determinants. Table III A contains the fixed-node energies extrapolated to unit norm from the data given in Figure 3 and the remaining orbital sets not shown in the figure. We find that when using HF or B3LYP orbitals, there is a large degree of sensitivity in the fixed-node energy to both the quantum chemistry method and the size of the virtual orbital space used to construct the excited determinants. CISD in a space of 20 active orbitals is the worst, missing about 3.6 and 2.8% of the correlation energy for HF and B3LYP orbitals respectively. Including triple and quadruple excitations or using SOCI with 20 virtual orbitals (CISDTQ-20 and SOCI-20 in the plot), or enlargening the space of double excitations to 50 virtual orbitals (CISD-50), gives a noticeable improvement in energy. This amounts to a recovery of between 1.4% and 1.7% for HF orbitals, and between 1.0% and 1.3% for B3LYP orbitals in the correlation energy. Lastly, CISDTQ and SOCI with 50 virtual orbitals give the best results (and largely indistinguishable results), missing approximately 0.6% and 0.8% of the correlation energy for both the HF and B3LYP orbitals.

Looking now at the results obtained using SOCI orbitals, we see a qualitatively different picture. Here, we can separate the convergence behaviors into two classes: those containing just singles and doubles (CISD), and those that consider higher-order excitations (CISDTQ and SOCI). The CISD converges to approximately 98.4% regardless of the size of the virtual orbital space, and does so rapidly but nonlinearly in the limit that we include all determinants. All other methods that include higher order excitations–CISDTQ explicitly and SOCI implicitly–converge to approximately 99.5% of the correlation energy, again independent of the size of the virtual space. We note that all these methods converge nearly linearly to this result and all with approximately the same slope, in contrast to the CISD set of determinants.

Method	CISD	CISDTQ	SOCI
HF-20	-11.0876(2) [96.4]	-11.0924(3) [97.6]	-11.0944(3) [98.1]
HF-50	-11.0933(2) [97.8]	-11.0996(3) [99.3]	-11.0998(1) [99.4]
CASSCF-20	-11.0911(2) [97.3]	-11.0945(2) [98.1]	-11.0959(2) [98.4]
CASSCF-50	-11.0944(2) [98.1]	-11.0995(3) [99.3]	-11.0993(1) [99.3]
MP2NO-20	-11.0945(1) [98.1]	-11.0980(2) [98.9]	-11.0982(3) [99.0]
MP2NO-50	-11.0952(2) [98.3]	-11.0990(3) [99.2]	-11.0989(1) [99.2]
PBE-20	-11.0911(2) [97.3]	-11.0953(2) [98.3]	-11.0964(3) [98.6]
PBE-50	-11.0946(1) [98.1]	-11.0996(3) [99.3]	-11.0998(2) [99.4]
B3LYP-20	-11.0908(2) [97.2]	-11.0952(2) [98.3]	-11.0961(3) [98.5]
B3LYP-50	-11.0948(2) [98.2]	-11.0992(3) [99.2]	-11.0997(2) [99.4]
SOCI-20	-11.0957(1) [98.4]	-11.1002(2) [99.5]	-11.1006(3) [99.6]
SOCI-50	-11.0962(2) [98.5]	-11.1005(2) [99.5]	-11.1006(1) [99.6]

TABLE III: Extrapolated energies of the carbon dimer at the equilibrium bond length from multi-determinant DMC calculations using orbitals generated from a selection of methods. All quantities reported correspond to extrapolations of the DMC energies with the norm of the truncated wavefunction included in the MSD expansion. Refer to the text for a description of the abbreviations. The percentage of the correlation energy recovered by each method is also presented.

B. Stretched Configuration

In this section, we will repeat the analysis we did for the equilibrium dimer, however focusing more on the qualitative/quantitative differences emerging in the stretched case. In this case there is a stronger multi-reference character in the ground state wavefunction. If we attempt to describe this system perturbatively from a single reference configuration, we should expect to see much more sensitivity to the starting wavefunction ansatz and number/type of included excitations than in the equilibrium dimer.

Table III B shows a summary of the DMC energies obtained using single determinant wavefunctions with HF, B3LYP and SOCI orbital sets. At the single determinant level, we find no significant qualitative or quantitative change from the equilibrium configuration in

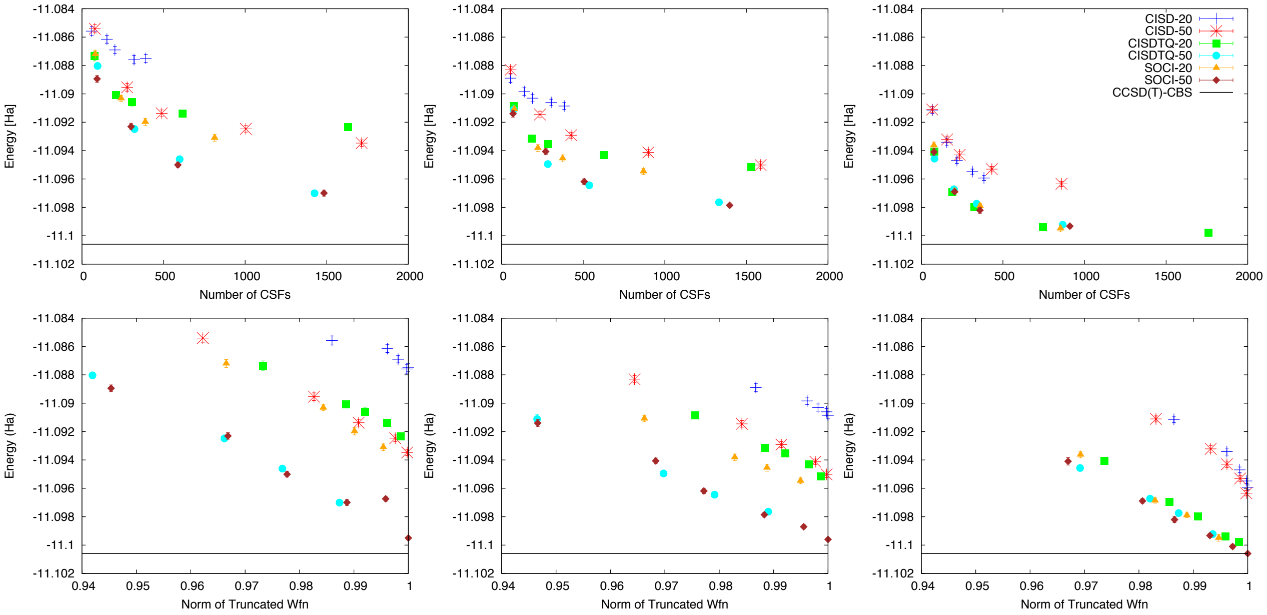

FIG. 3: (Color online) DMC energy of the carbon dimer at equilibrium as a function of the number of CSF's (top) and norm of the MSD wavefunction (bottom) using HF orbitals (first column), B3LYP orbitals (second column), and SOCI orbitals (last column). The different colors represent the different quantum chemistry methods used for choosing the excited determinants. The CCSD(T)-CBS energy is shown for comparison.

the dependence of the fixed-node energy on the choice of single particle orbitals. As in the equilibrium case, we can recover about 88.4% of the correlation energy by using SOCI or B3LYP orbitals. Hartree-Fock is again worse than these two choices of orbitals, but only by about 1% of the correlation energy.

As in the equilibrium case, we now look at the impact of orbital choice on a MSD expansion based on SOCI(8,8) with 50 virtual orbitals, results are shown in Figure 4. Despite the fact that this is a more complicated problem, our considered orbital sets all recover around 99% of the correlation energy. Specifically, B3LYP and SOCI orbitals recover almost the same amount of correlation energy as in the equilibrium case (between 99.3% and 99.6%). Even HF orbitals recover 98.8% of the correlation energy (though less than the 99.4% in equilibrium). Additionally, as we look at the rate of convergence of the fixed-node energy to the full SOCI(8,8) set of determinants, we find that once again, the SOCI(orbitals) are more rapidly convergent, followed by B3LYP and HF. Notice how in this case only several hundred determinants are needed to obtain results that are better than CCSD(T)-CBS, which is a

Method	Total Energy (Ha)	% CE
SD-DMC-HF	-10.9407(2)	87.5
SD-DMC-B3LYP	-10.9440(2)	88.5
SD-DMC-SOCI	-10.9439(2)	88.4
CCSD(T)-CBS	-10.97725	98.0
Estimated-Exact	-10.9841	100.0

TABLE IV: Summary of energies of the carbon dimer at a stretched configuration from DMC calculations using orbitals generated from a selection of methods. Refer to the text for a description of the abbreviations. The percentage of the correlation energy recovered by each method is also presented.

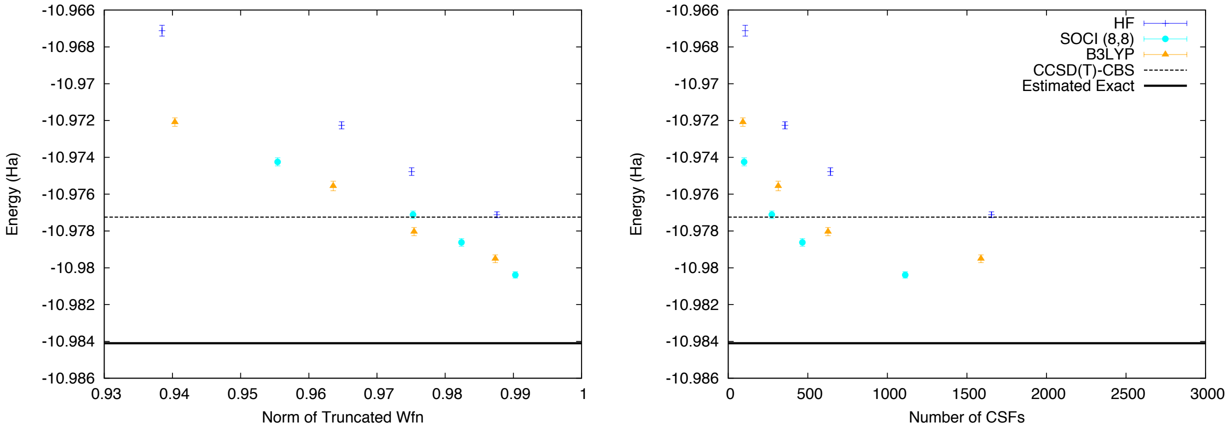

FIG. 4: (Color online) DMC energy of the carbon dimer in the stretched configuration as a function of the norm of the truncated trial wave function (left) and as a function of the number of CSFs (right). Results are shown for HF, B3LYP and SOCI orbital sets. CCSD(T)-CBS and estimated exact results are also when for comparison.

sign of the stronger multi-reference character of the electronic state.

Figure 5 shows the convergence of the fixed-node energy with respect to number of CSF's (top row) and norm of CI wavefunction (bottom row) for HF orbitals (first column), B3LYP orbitals (second column), and SOCI orbitals (last column), Table III B shows a summary of the extrapolated DMC energies. As expected, selecting configurations using SOCI leads to noticeably optimal results in all orbital sets. They also lead to similar rates of convergence

Method	CISD	CISDTQ	SOCI
HF-20	-10.9680(2) [95.4]	-10.9719(4) [96.5]	-10.9738(4) [97.0]
HF-50	-10.9740(2) [97.1]	-	-10.9799(3) [98.8]
B3LYP-20	-10.9708(2) [96.2]	-10.9756(2) [97.6]	-10.9769(3) [97.9]
B3LYP-50	-10.9748(1) [97.3]	-10.9816(4) [99.3]	-10.9818(4) [99.3]
SOCI-20	-10.9747(2) [97.3]	-10.9803(3) [98.9]	-10.9819(3) [99.4]
SOCI-50	-10.9755(2) [97.5]	-10.9813(3) [99.2]	-10.9824(3) [99.5]

TABLE V: Summary of energies of the carbon dimer at a stretched configuration from DMC calculations using orbitals generated from a selection of methods. Refer to the text and the caption of figure III A for a description of the abbreviations. The percentage of the correlation energy recovered by each method is also presented.

with respect to the number of CSFs included in the wavefunction and to similar extrapolated energies. On the other hand, there is a strong variation on the amount of correlation energy recovered when less aggressive configuration selection algorithms are chosen. This is very pronounced when HF and B3LYP orbital sets are used.

IV. DISCUSSION

Several important observations can be made from the two examples presented above.

First, the inclusion of several hundred configurations leads to large improvement in the percentage of correlation energy recovered relative to single slater jastrow wavefunctions. This allows us to recover at least 95% of the correlation for both the equilibrium and stretched geometries for all methods we considered, over the 89% we saw with single determinant wavefunctions. In trying to recover the remaining 5% however, we observed that the fixed-node energy from the MSD wavefunction was sensitive to the choice of orbitals and method used to generate the CSF's. Both examples led to qualitatively similar results, where SOCI provided the optimal orbital choice, followed by B3LYP and with HF providing the worst choice. This is expected given the level of sophistication of each method and the level at which each method treats correlation. The speed of convergence of the energy with the number of configurations included in the MSD expansion also varied significantly

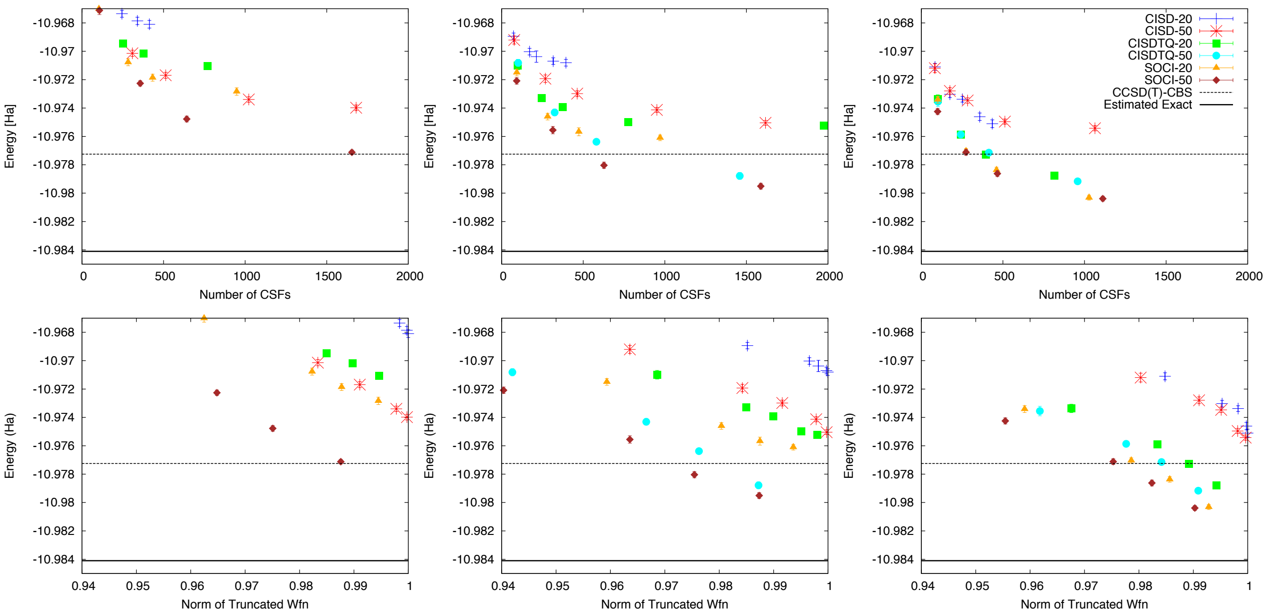

FIG. 5: (Color online) DMC energy of the carbon dimer at the strstched configuration as a function of the number of CSF's (top) and norm of the MSD wavefunction (bottom) using HF orbitals (first column), B3LYP orbitals (second column), and SOCI orbitals (last column). The different colors represent the different quantum chemistry methods used for choosing the excited determinants. The CCSD(T)-CBS and estimated exact energies are shown for comparison.

depending on the orbital set and the configuration selection algorithm. On the other hand, regardless of the quality of the orbitals used, the extrapolated DMC energies were very similar and quite accurate when an aggressive configuration selection scheme (SOCI) was used. The existence of stronger multi-reference character in the stretched configuration did not led to any significant differences in the overall dependence of the energy with orbital set and configuration selection. Even at the single determinant level both configurations resulted in quantitatively similar results.

Second, we observed another obvious benefit of using "good" orbitals in QMC calculations other than obtaining lower energies. We observed that convergence of the fixed-node energy to the full truncated CI space limit was far more smooth and linear in the case of good orbitals than with poor orbitals. This is of extreme importance, because not only can we get away with using fewer CSF's to achieve a given fixed-node error in a QMC calculation, but we can save a lot of computer time by being able to meaningfully extrapolate to large determinant set limits with just a few CSF's.

From this analysis it is clear that both orbital optimization and configuration selection are important aspects in the construction of accurate MSD wavefunctions in QMC. While we can rely on high level quantum chemistry methods for both tasks in small molecular systems, this is clearly not possible for larger molecules and bulk systems. In this case we must rely on alternative methods to perform these tasks, ideally using methods based entirely on QMC. There are two simple alternatives for orbital set generation. The simplest approach is to perform an optimization of the orbital set at the VMC level using a multideterminant trial wave function. This is typically restricted to MSD expansions over small active space [16, 26, 27], since the choice of configurations is frozen throughout the process. The second approach involves the use of natural orbitals obtained from QMC calculations. While the calculation of natural orbitals requires the calculation of the 1-particle reduced density matrix, which can be computationally expensive, the resulting orbitals can be very accurate and the calculation can be performed self-consistently with increasingly more complicated trial wave-functions at each step. We are currently investigating both alternatives. The results will be presented in a future publication.

The selection of determinant configurations using QMC, given some orbital set, has received considerably less attention in the community so far. In principle, it is straightforward to use VMC optimization to select important configurations. The main disadvantage is the need to perform an optimization process including all possible configurations simultaneously, which given the negligibly small number of important configurations in an otherwise exponentially large configuration set leads to both inefficiency and a low chance of success in practice. Algorithms that perform this task perturbatively, without the need to explicitly optimize all the configurations simultaneously, are currently being considered. The recently introduced self-healing algorithm [36, 37] offers another alternative for both the configuration selection but also for the optimization of the resulting linear parameters at the DMC level. Unfortunately, the method suffers from the same problem as a direct VMC optimization of needing to explicitly treat all possible configurations directly in the DMC calculation. Nonetheless, the method offers important insight into the optimization of wavefunctions at the DMC level, which we believe will be influential in the development of new configuration selection algorithms in the future.

V. CONCLUSIONS

In this paper, we have analyzed the the effects that various combinations of orbital set choice, configuration selection method, and number of included configurations has on the fixed-node DMC energy. Specifically, we found that the convergence of the trial wavefunction with respect to added configurations can be dramatically improved through the joint choices of orbital sets that take into account electronic correlation, and through select inclusion of highly excited determinants through methods like SOCI.

Given the gains we see at this level, we believe it is necessary to be able to jointly optimize orbital sets and intelligently choose configurations without the aid of high-level quantum chemistry calculations, since larger systems and solids are currently beyond the scope of these quantum chemistry methods. We believe that reasonable modifications of currently extant methods like VMC optimization with many parameters and self-healing, as well as self-consistent hybrid approaches described in our previous discussion, are the most promising avenues towards accomplishing this goal. Eventually, it is hoped that algorithmic advancements like the aforementioend will render large scale multideterminant calculations as robust and far more accurate than a routine Slater-Jastrow QMC calculation.

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Acknowledgments

This work was supported through the Predictive Theory and Modeling for Materials and Chemical Science program by the Office of Basic Energy Sciences (BES), Department of Energy (DOE). This work was performed under the auspices of the US DOE by LLNL under Contract DE-AC52-07NA27344.